Crystal growth and characterization of solvated organic charge-transfer complexes built on TTF and 9-dicyanomethylenefluorene derivatives

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Electronic Supplementary Information (ESI)

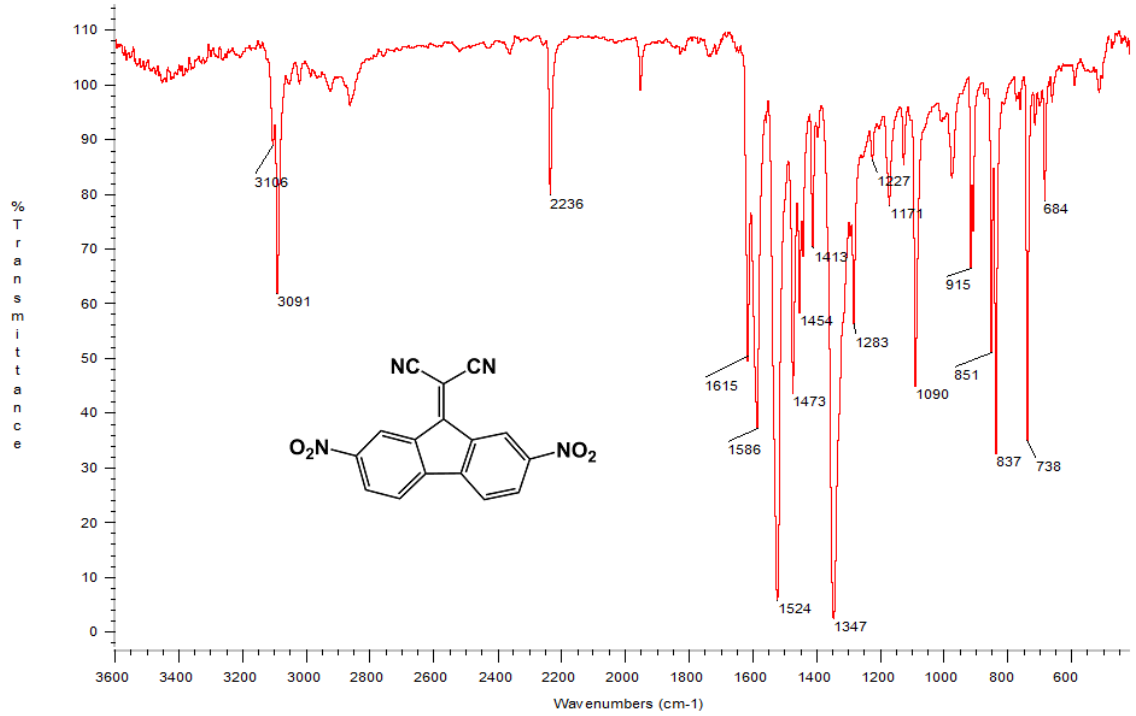


Fig. S1 FTIR spectrum of acceptor DDF

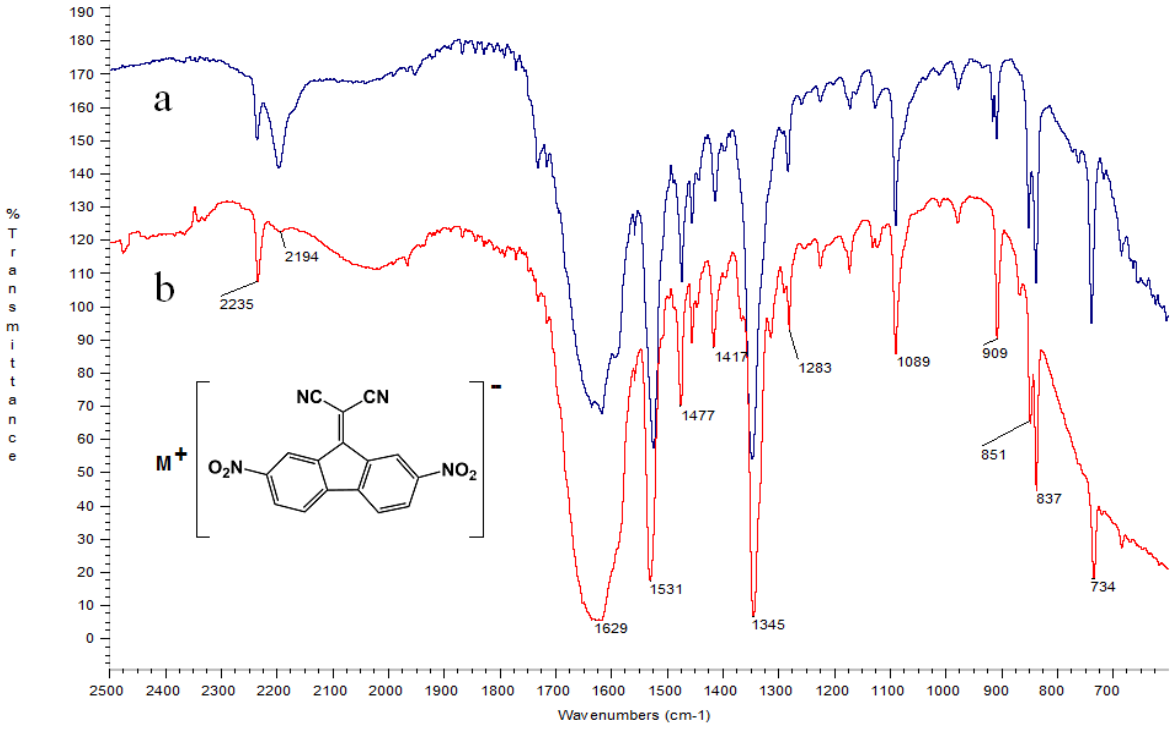


Fig. S2 FTIR spectra of DDF^-salts. (**a**) $M^+ = Li^+$, (**b**) $M^+ = Na^+$

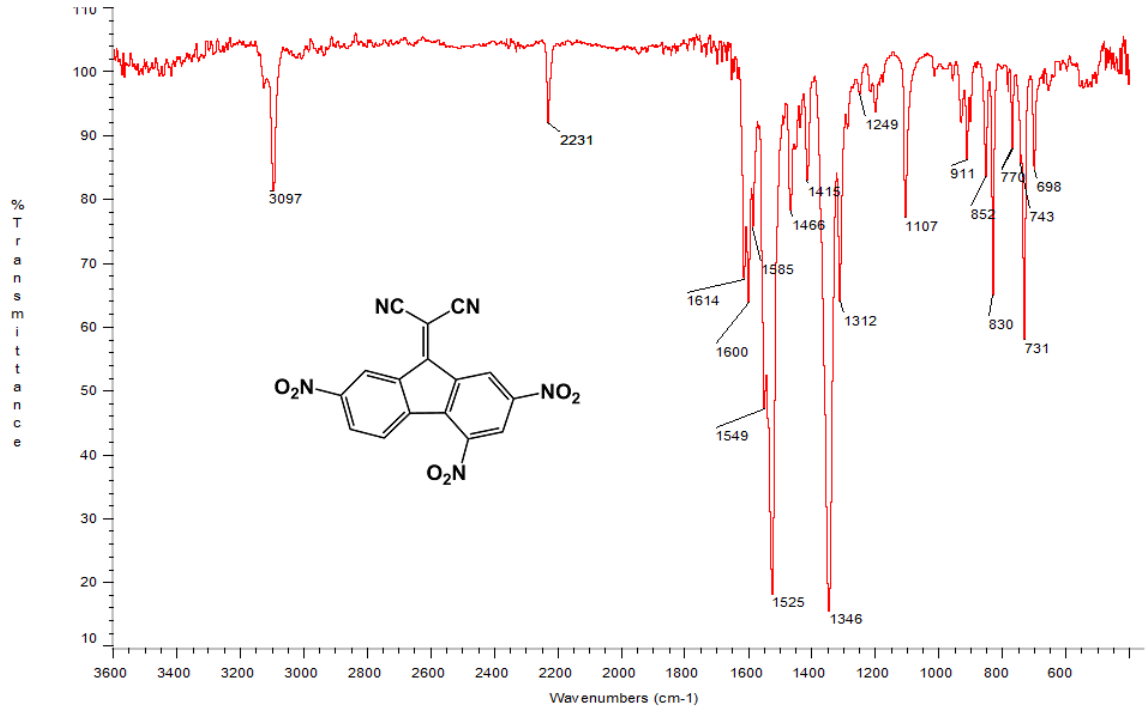


Fig. S3 FTIR spectrum of acceptor DTF

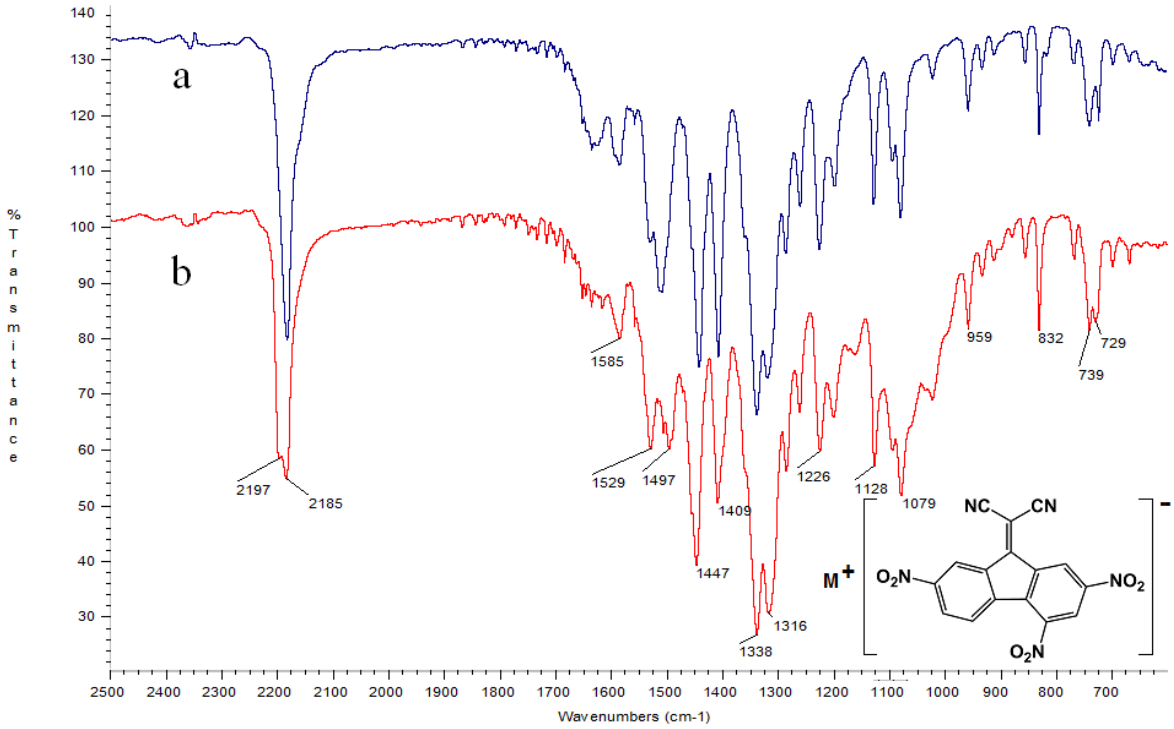


Fig. S4 FTIR spectra of DTF^- salts. (**a**) $M^+ = Li^+$, (**b**) $M^+ = Na^+$

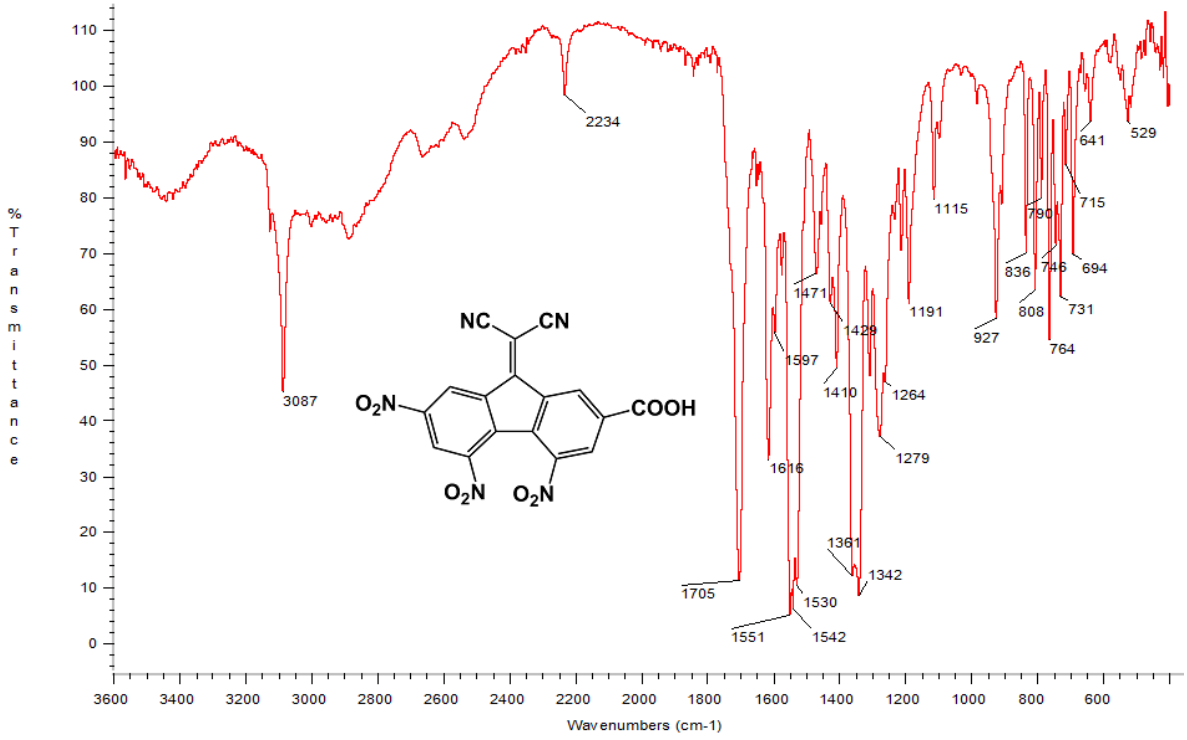


Fig. S5 FTIR spectrum of acceptor DC2TF

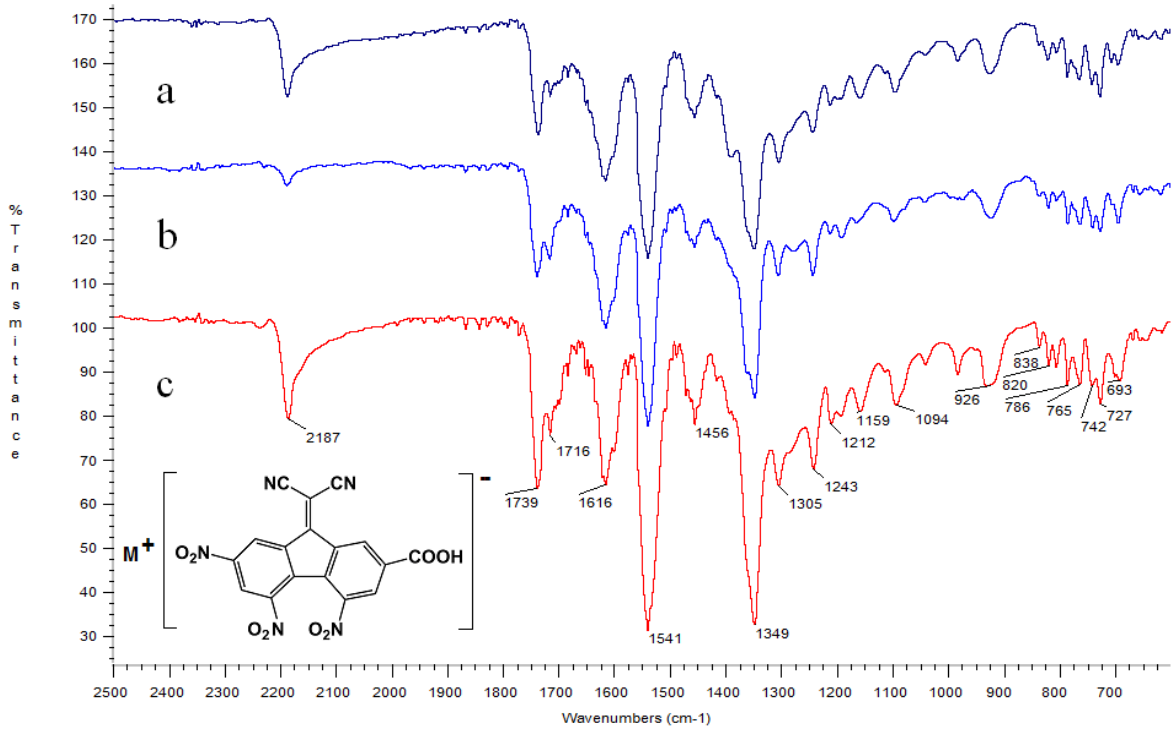


Fig. S6 FTIR spectra of $DC2TF^-$ salts. (**a**) $M^+ = Li^+$, (**b**) $M^+ = Na^+$, (c) $M^+ = K^+$

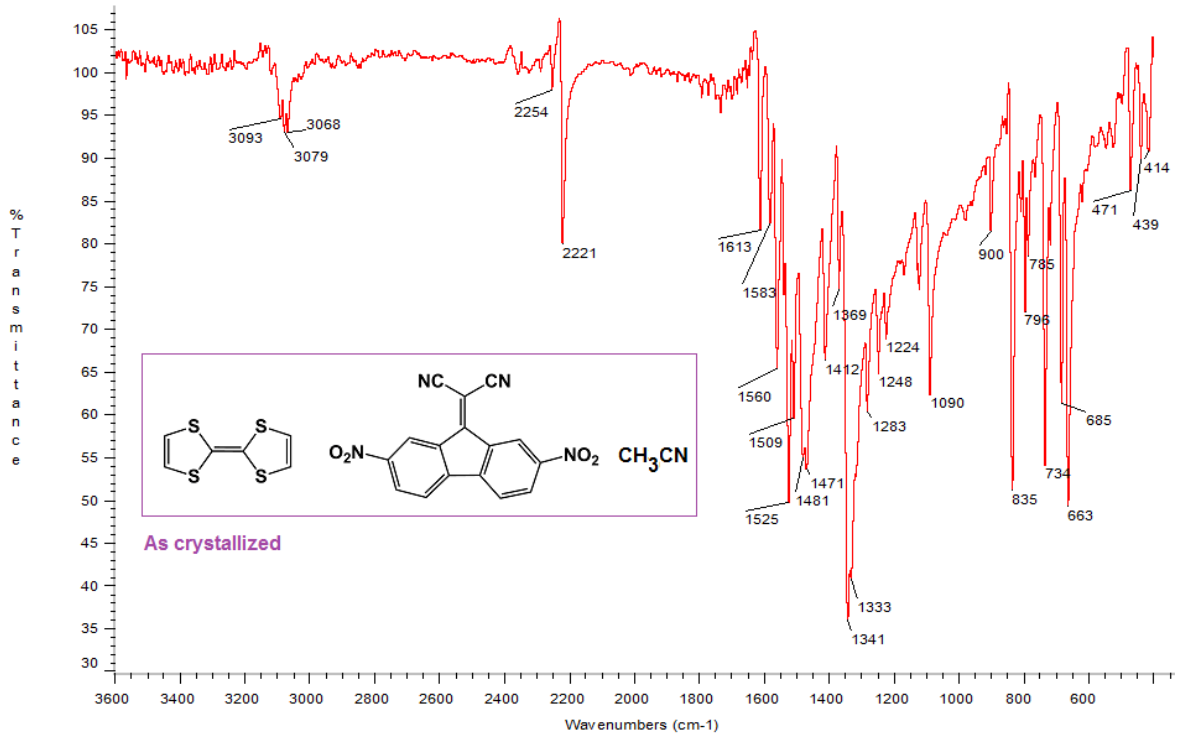


Fig. S7 FTIR of compound **1**, just after crystallization

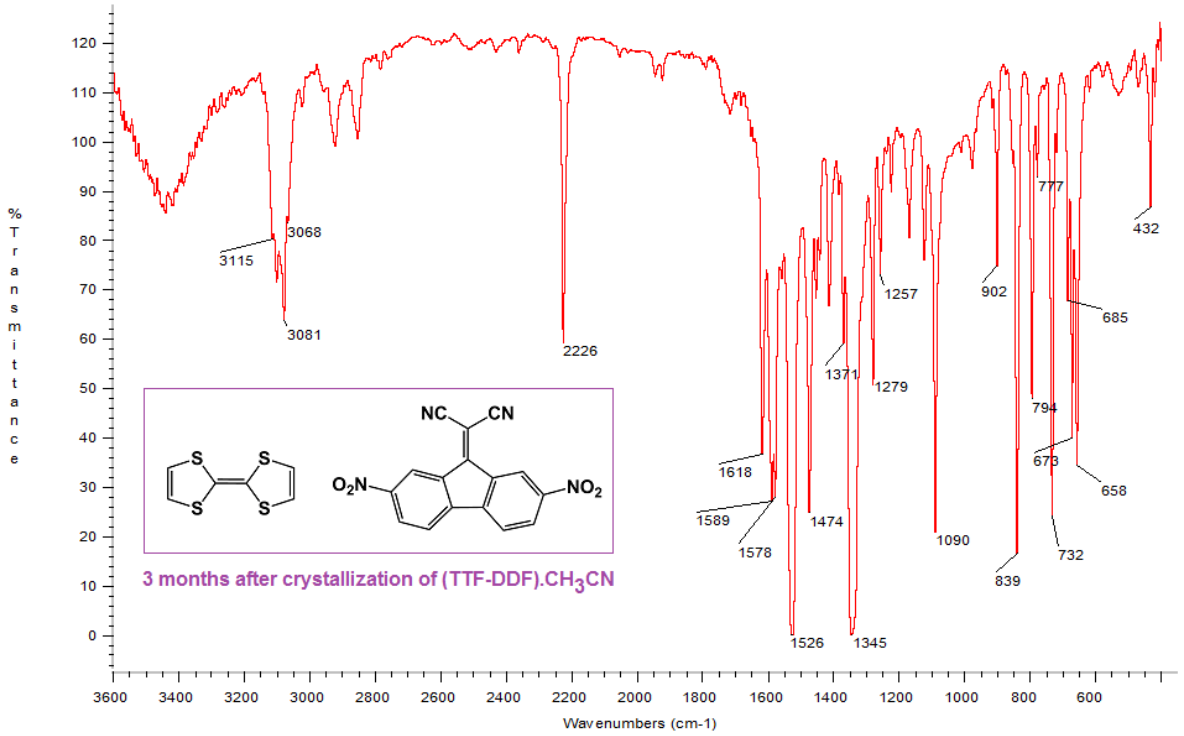


Fig. S8 FTIR of compound **1**, three months after crystallization

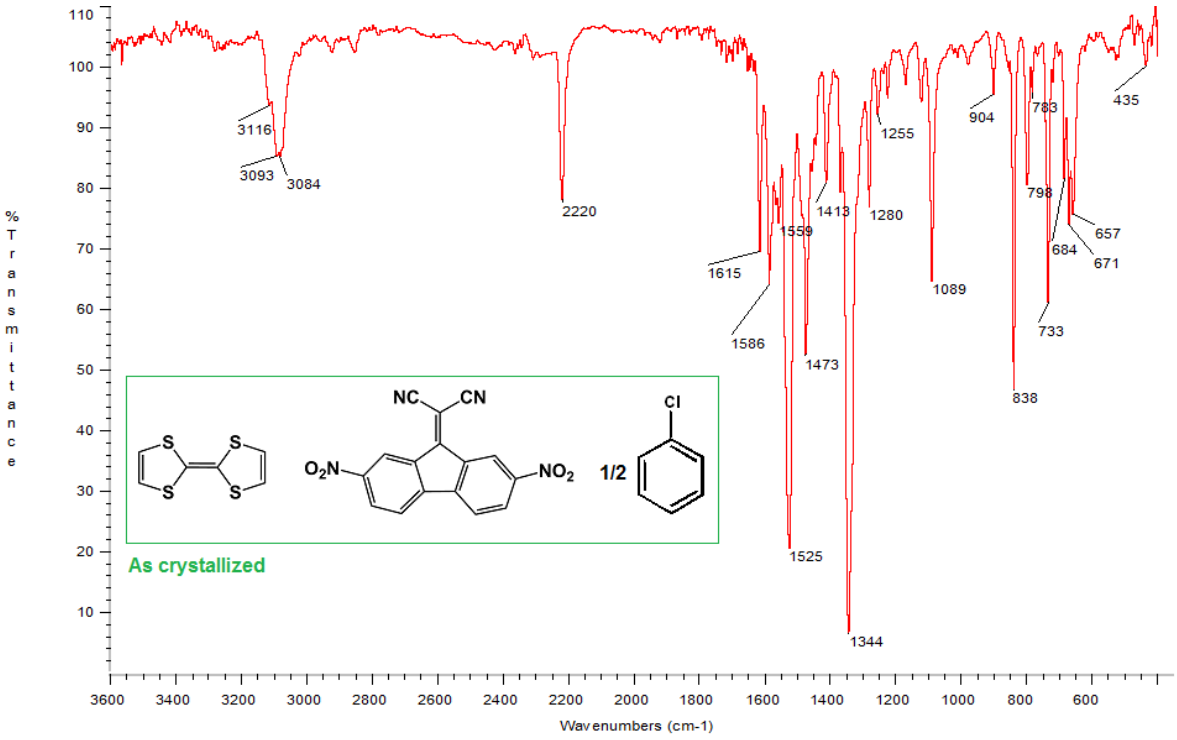


Fig. S9 FTIR of compound **2**, just after crystallization

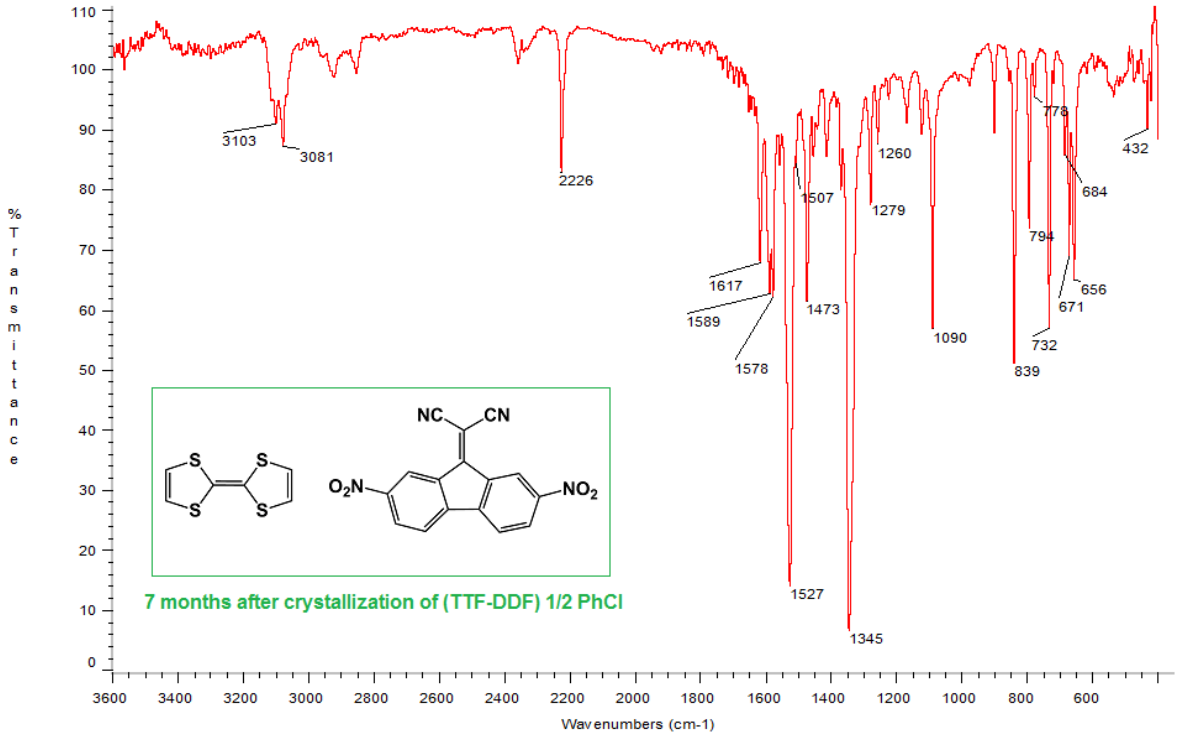


Fig. S10 FTIR of compound **2**, seven months after crystallization

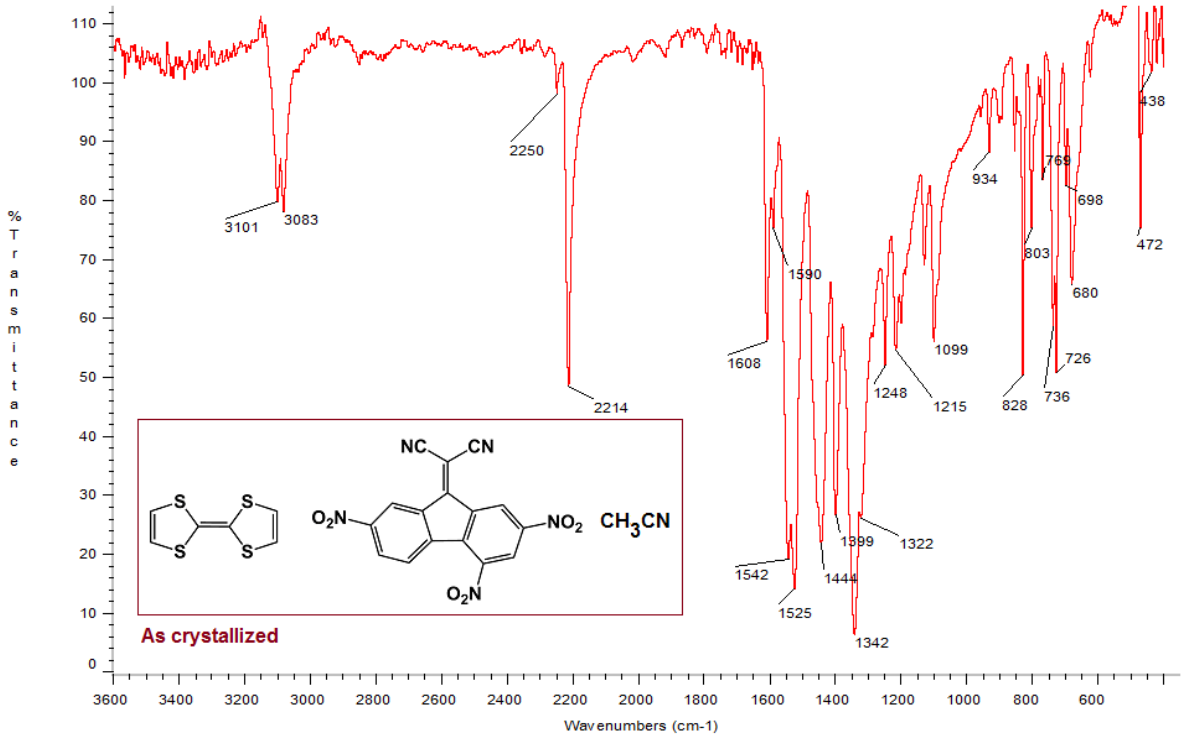


Fig. S11 FTIR of compound **3**, just after crystallization

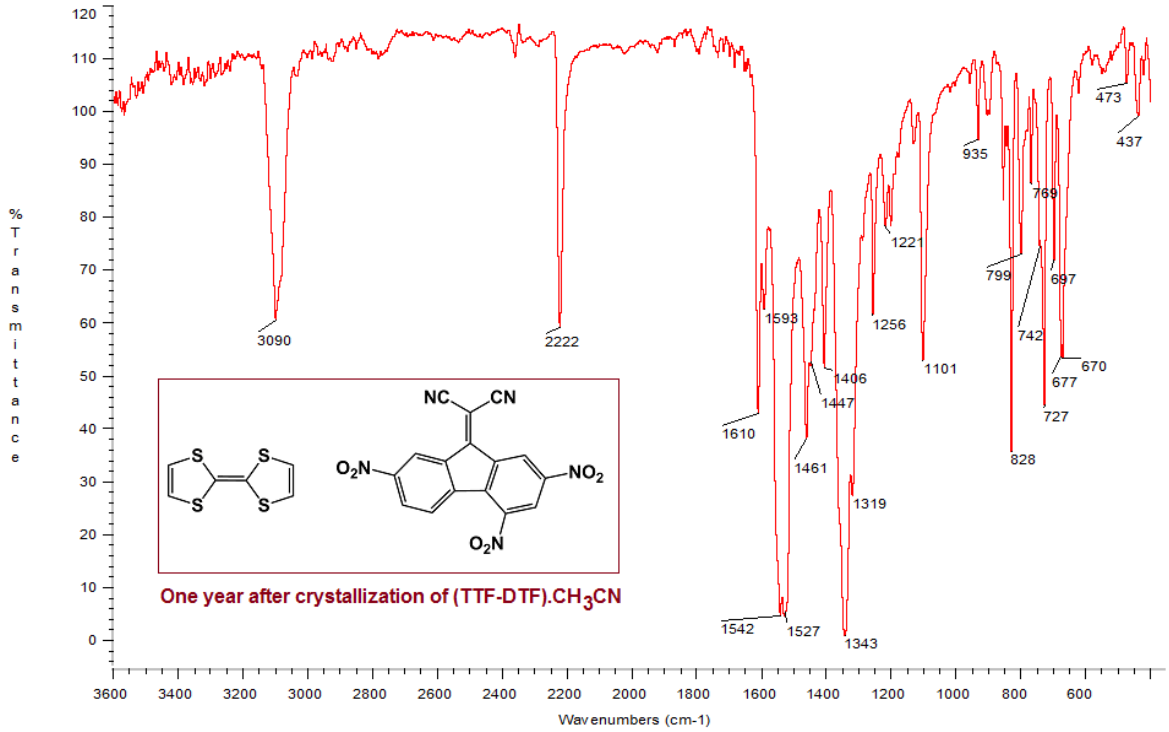


Fig. S12 FTIR of compound **3**, one year after crystallization

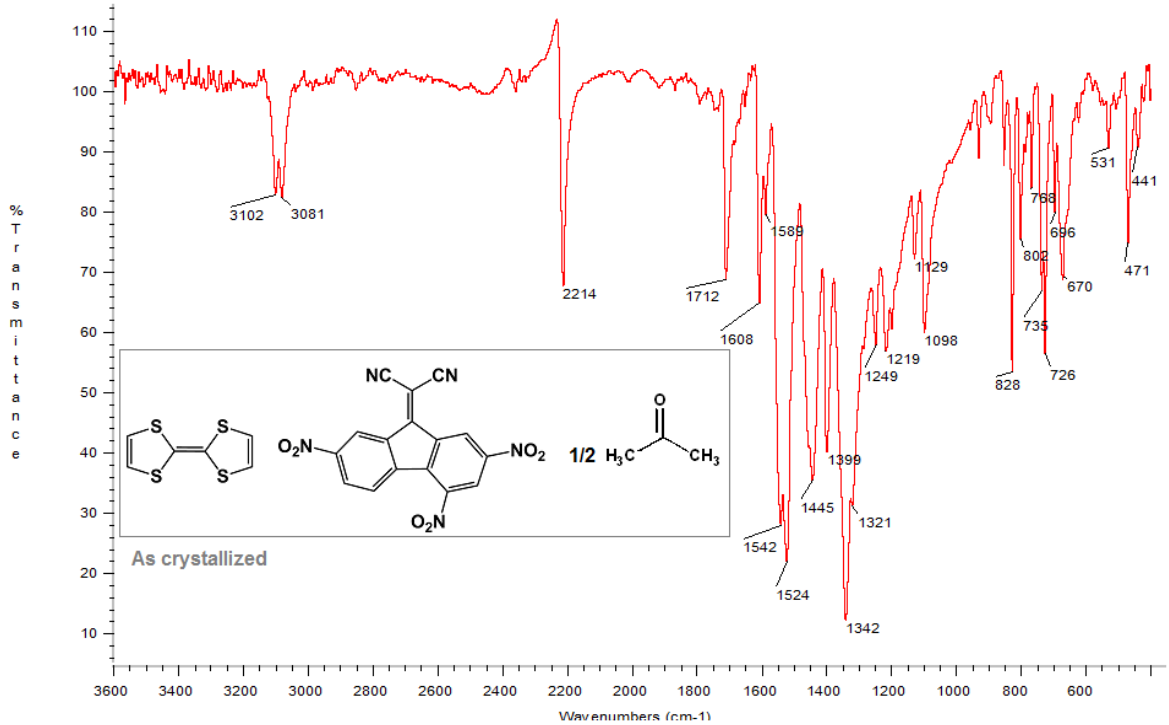


Fig. S13 FTIR of compound **4**, just after crystallization

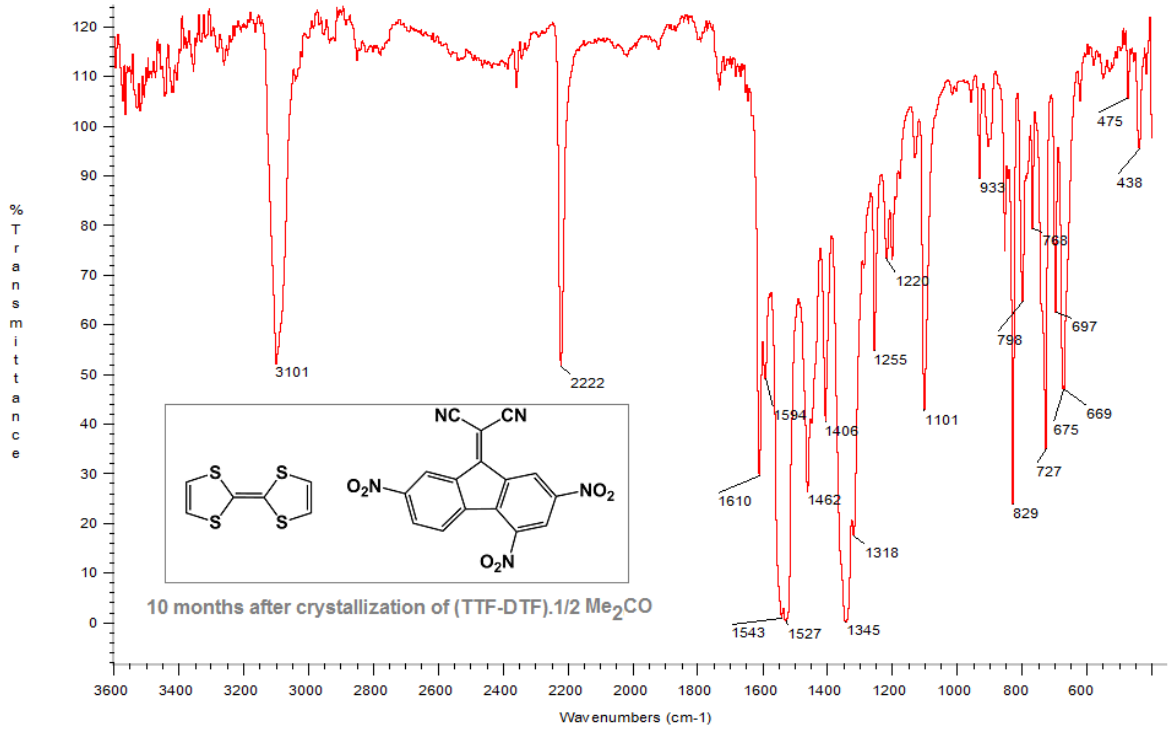


Fig. S14 FTIR of compound **4**, ten months after crystallization

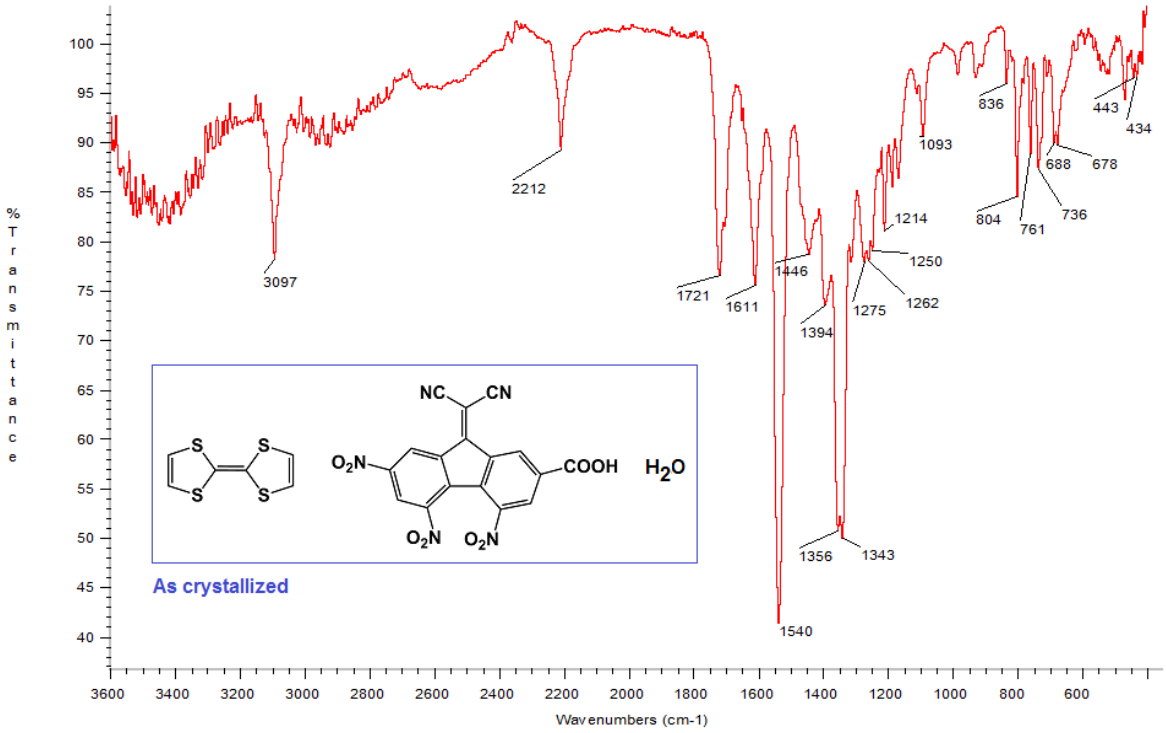


Fig. S15 FTIR of compound **5**

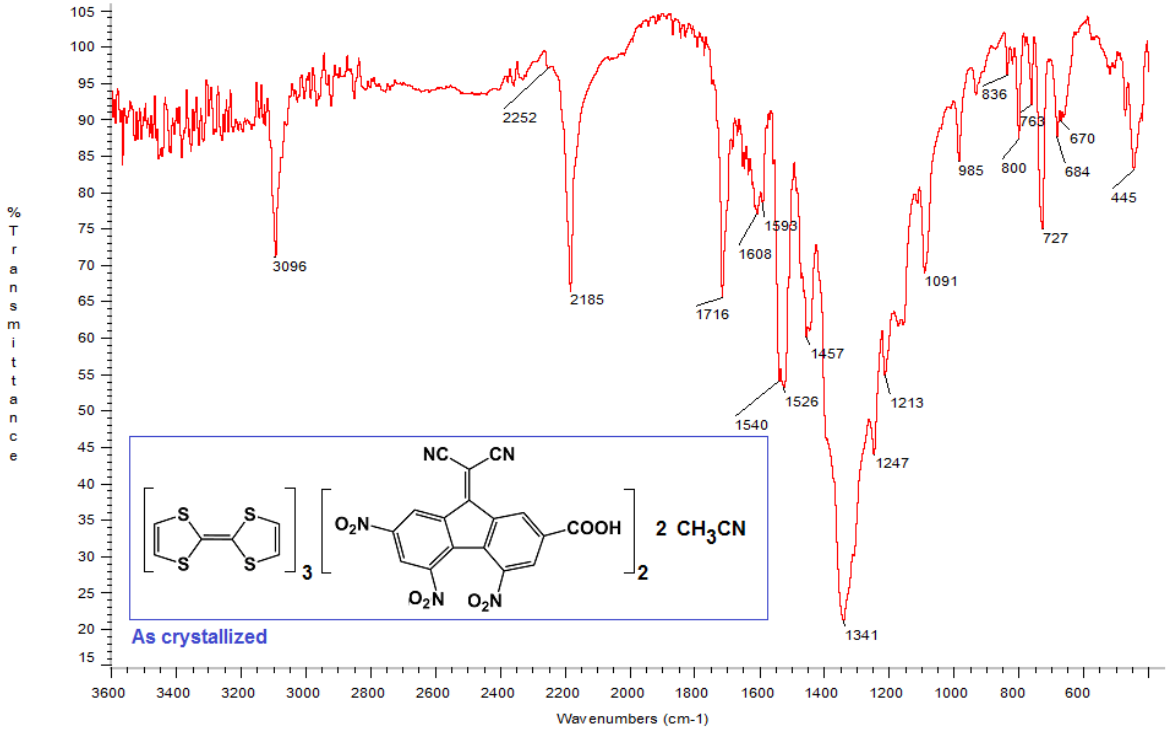


Fig. S16 FTIR of compound **6**

Table S17. Crystal data and structure refinement for complex **1**

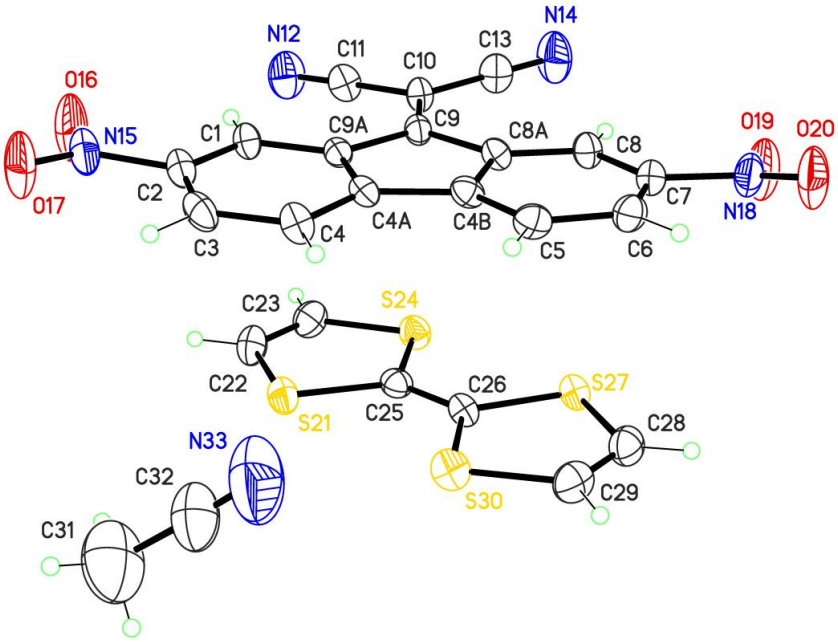
Identification code	**(TTF-DDF).CH_3CN**	
Empirical formula	C_{24} H_{13} N_5 O_4 S_4	
Formula weight	563.63	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 7.141(2) Å	α= 90°.
	b = 17.151(4) Å	β= 99.18(3)°.
	c = 20.891(5) Å	γ = 90°.
Volume	2525.6(12) Å^3	
Z	4	
Density (calculated)	1.482 Mg/m^3	
Absorption coefficient	0.418 mm^{-1}	
F(000)	1152	
Crystal size	0.60 x 0.14 x 0.10 mm^3	
θ range for data collection	1.544 to 23.999°.	
Index ranges	-8<=h<=2, -1<=k<=19, -23<=l<=23	
Reflections collected	5355	
Independent reflections	3950 [R_{int} = 0.0658]	
Completeness to θ = 23.999°	99.8 %	
Absorption correction	ψ-scans (0.378 – 0.516)	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3950 / 0 / 336	
Goodness-of-fit on F^2	1.096	
Final R indices [I>2σ(I)]	R_1 = 0.0664, wR_2 = 0.1564	
R indices (all data)	R_1 = 0.1038, wR_2 = 0.1773	
Extinction coefficient	0.0005(3)	
Largest diff. peak and hole	0.450 and -0.364 e.Å^{-3}	

Table S18. Hydrogen bonds for **1** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1)-H(1A)...N(12)	0.93	2.56	3.361(8)	144.0
C(6)-H(6A)...O(20)#1	0.93	2.58	3.373(7)	143.7
C(8)-H(8A)...N(14)	0.93	2.61	3.405(8)	144.1

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z+1

Refinement for this complex was standard and carried out without restrictions nor constrictions. All H atoms were included in calculated positions and refined as riding to their carrier C atoms.



Alert level B

THETM01_ALERT_3_B	The value of sine(theta_max)/wavelength is less than 0.575
	Calculated sin(theta_max)/wavelength = 0.5723
PLAT031_ALERT_4_B	Refined Extinction Parameter within Range ..... 1.667 Sigma

Alert level C

PLAT242_ALERT_2_C	Low	Ueq as Compared to Neighbors for ..... N15 Check
PLAT242_ALERT_2_C	Low	Ueq as Compared to Neighbors for ..... N18 Check
PLAT244_ALERT_4_C	Low	'Solvent' Ueq as Compared to Neighbors of C32 Check
PLAT340_ALERT_3_C	Low Bond Precision on C-C Bonds	0.0076 Ang.
PLAT906_ALERT_3_C	Large K value in the Analysis of Variance	7.200 Check
PLAT911_ALERT_3_C	Missing # FCF Refl Between THmin & STh/L= 0.572	8 Report

Fig. S19 ORTEP view of complex **1** (asymmetric unit; 30% probability level) and checkCIF/PLATON report (Alert level G omitted)

Table S20. Crystal data and structure refinement for complex **2**

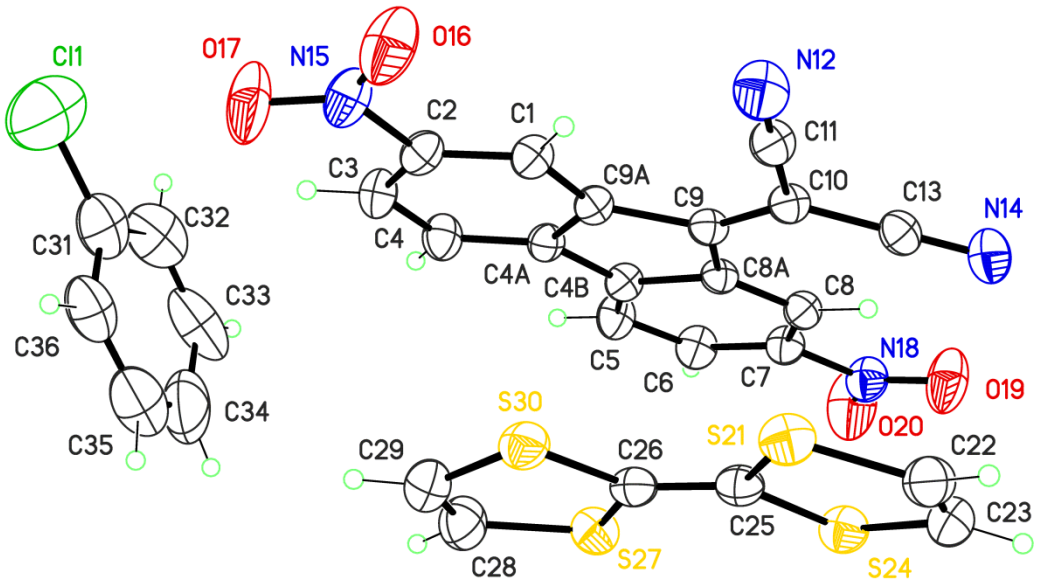
Identification code	**(TTF-DDF).0.5PhCl**	
Empirical formula	C_{25} $H_{12.50}$ $Cl_{0.50}$ N_4 O_4 S_4	
Formula weight	578.85	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 7.3769(11) Å	α= 81.218(7)°.
	b = 9.3811(9) Å	β= 88.805(10)°.
	c = 18.9293(19) Å	γ = 75.958(10)°.
Volume	1255.8(3) Å^3	
Z	2	
Density (calculated)	1.531 Mg/m^3	
Absorption coefficient	0.473 mm^{-1}	
F(000)	590	
Crystal size	0.44 x 0.18 x 0.10 mm^3	
θ range for data collection	2.178 to 24.991°.	
Index ranges	-8<=*h*<=3, -11<=*k*<=10, -22<=*l*<=22	
Reflections collected	6313	
Independent reflections	4400 [R_{int} = 0.0244]	
Completeness to θ = 24.991°	99.7 %	
Absorption correction	ψ-scans (0.316 – 0.350)	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4400 / 86 / 370	
Goodness-of-fit on F^2	1.014	
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0408, wR_2 = 0.0921	
R indices (all data)	R_1 = 0.0762, wR_2 = 0.1098	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.178 and -0.301 e.Å^{-3}	

Table S21. Hydrogen bonds for **2** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1)-H(1A)...N(12)	0.93	2.63	3.427(4)	144.5
C(8)-H(8A)...N(14)	0.93	2.65	3.451(4)	144.6
C(22)-H(22A)...O(19)#2	0.93	2.48	3.098(4)	124.5
C(23)-H(23A)...O(19)#2	0.93	2.65	3.181(4)	117.0
C(32)-H(32A)...O(16)#3	0.93	2.59	3.189(15)	123.0

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1 #2 -x,-y,-z #3 x,y+1,z

The chlorobenzene molecule is placed close to an inversion centre, and was refined with a s.o.f. constrained to ½. The geometry and thermal behaviour for this molecule were restrained: all C–C bond lengths were restrained to 1.39(1) Å and the six-membered ring was restrained to be flat (standard *FLAT* command in *SHELXL*). Chlorobenzene C atoms (C31…C36) were also constrained to approximate an isotropic shape and to have similar ADP's (standard *ISOR* and *SIMU* commands in *SHELXL*). All H atoms were included in calculated positions and refined as riding to their carrier C atoms.



Alert level C

PLAT242_ALERT_2_C	Low	Ueq as Compared to Neighbors for	N15 Check
PLAT242_ALERT_2_C	Low	Ueq as Compared to Neighbors for	N18 Check
PLAT250_ALERT_2_C	Large U3/U1 Ratio for Average U(i,j) Tensor		2.1 Note
PLAT340_ALERT_3_C	Low Bond Precision on C-C Bonds		0.0041 Ang.
PLAT480_ALERT_4_C	Long H...A H-Bond Reported H8A .. N14 ..		2.65 Ang.
PLAT480_ALERT_4_C	Long H...A H-Bond Reported H23A .. O19 ..		2.65 Ang.
PLAT906_ALERT_3_C	Large K value in the Analysis of Variance		2.359 Check
PLAT911_ALERT_3_C	Missing # FCF Refl Between THmin & STh/L= 0.594		13 Report

Fig. S22 ORTEP view of complex **2** (asymmetric unit; 30% probability level) and checkCIF/PLATON report (Alert level G omitted)

Table S23. Crystal data and structure refinement for complex **3**

Identification code	**(TTF-DTF).CH_3CN**	
Empirical formula	C_{24} H_{12} N_6 O_6 S_4	
Formula weight	608.64	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pbca*	
Unit cell dimensions	*a* = 7.1635(16) Å	α= 90°.
	b = 19.881(4) Å	β= 90°.
	c = 37.705(8) Å	γ = 90°.
Volume	5370(2) $Å^3$	
Z	8	
Density (calculated)	1.506 Mg/m^3	
Absorption coefficient	0.406 mm^{-1}	
F(000)	2480	
Crystal size	0.40 x 0.40 x 0.10 mm^3	
θ range for data collection	2.049 to 25.003°.	
Index ranges	-8<=*h*<=1, -23<=*k*<=1, -1<=*l*<=44	
Reflections collected	6049	
Independent reflections	4730 [R_{int} = 0.0273]	
Completeness to θ = 25.003°	100.0 %	
Absorption correction	ψ-scans (0.200 – 0.240)	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4730 / 111 / 417	
Goodness-of-fit on F^2	1.029	
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0570, wR_2 = 0.1404	
R indices (all data)	R_1 = 0.1039, wR_2 = 0.1647	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.361 and -0.324 $e.Å^{-3}$	

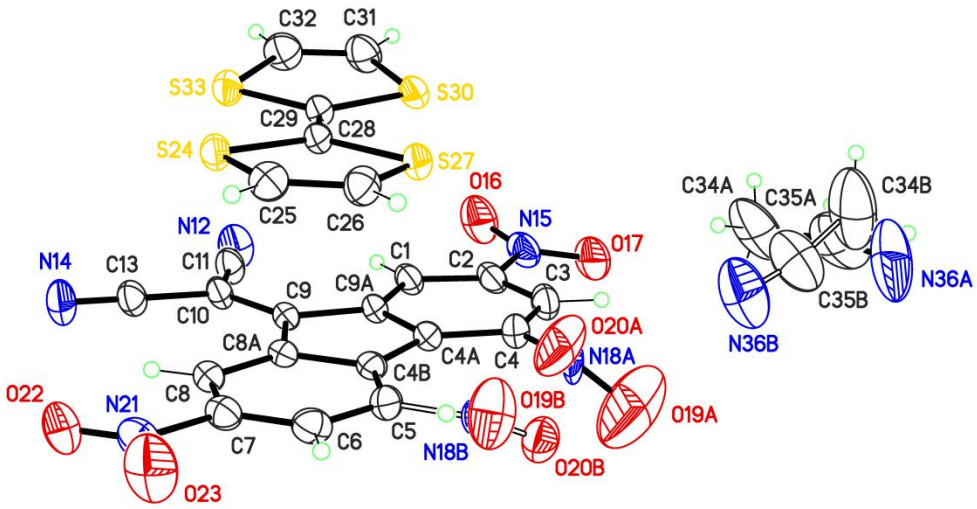
Table S24. Hydrogen bonds for **3** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)	
C(1)-H(1A)...N(12)	0.93	2.59	3.404(6)	146.2	
C(4)-H(4A)...O(20B)	0.93	2.09	2.795(8)	131.1	
C(5)-H(5A)...N(18A)	0.93	2.61	3.159(14)		118.3
C(5)-H(5A)...O(20A)	0.93	1.98	2.68(2)	131.6	
C(8)-H(8A)...N(14)	0.93	2.59	3.405(5)	146.4	
C(31)-H(31A)...O(16)#1	0.93	2.63	3.468(6)	150.8	
C(32)-H(32A)...O(19A)#2	0.93	2.41	3.309(18)		161.1
C(32)-H(32A)...O(20A)#2	0.93	2.50	3.225(13)		134.6
C(34A)-H(34A)...S(30)#3	0.96	2.86	3.62(2)	136.9	
C(34B)-H(34F)...N(36B)#1	0.96	2.59	3.46(3)	150.2	

Symmetry transformations used to generate equivalent atoms:
#1 x-1/2,y,-z+1/2 #2 -x+1/2,y-1/2,z #3 x+1/2,y,-z+1/2

In the acceptor molecule, nitro group bonded to C4 is disordered over two positions, N18A/O19A/O20A [sof = 0.317(6)] and N18B/O19B/O20B [sof = 1 - 0.317(6) = 0.683(6)], emulating C_2 local symmetry for this molecule. The geometry of these nitro groups was restrained, with C4–N18A and C5–N18B bond lengths restrained to 1.49(2) Å, and N–O bond lengths restrained to 1.21(2) Å.

Acetonitrile is disordered over a number of positions, and was modelled using two sites, C34A/C35A/N36A [sof = 0.248(8)] and C34B/C35B/N36B [sof = 1 - 0.248(8) = 0.752(8)]. The geometry was restrained in order to target sensible bond lengths and angles in both sites: C34A–C35A = 1.44(1) Å, C35A–N36A = 1.14(1) Å, C34A…N36A = 2.58(1) Å, and similar restraints for B site. All C,N atoms for acetonitrile were restrained to approximate isotropic displacement parameters and to have similar U_{ij} values (standard *ISOR* and *SIMU* commands in *SHELXL*). All H atoms were included in calculated positions and refined as riding to their carrier C atoms.



Alert level C

PLAT220_ALERT_2_C	Large Non-Solvent O Ueq(max)/Ueq(min) Range	3.1 Ratio
PLAT242_ALERT_2_C	Low Ueq as Compared to Neighbors for	N15 Check
PLAT242_ALERT_2_C	Low Ueq as Compared to Neighbors for	N21 Check
PLAT340_ALERT_3_C	Low Bond Precision on C-C Bonds	0.0055 Ang.
PLAT480_ALERT_4_C	Long H...A H-Bond Reported H31A .. O16 ..	2.63 Ang.
PLAT906_ALERT_3_C	Large K value in the Analysis of Variance	6.421 Check

Fig. S25 ORTEP view of complex **3** (asymmetric unit; 20% probability level) and checkCIF/PLATON report (Alert level G omitted)

Table S26. Crystal data and structure refinement for complex **4**

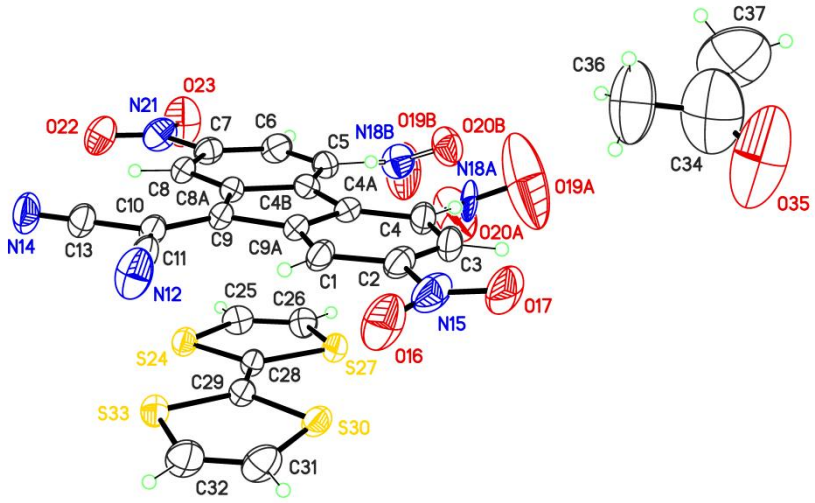
Identification code	**(TTF-DTF).0.5Me$_2$CO**	
Empirical formula	$C_{23.50}\,H_{12}\,N_5\,O_{6.50}\,S_4$	
Formula weight	596.62	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pbca*	
Unit cell dimensions	*a* = 7.1682(15) Å	α= 90°.
	b = 19.902(6) Å	β= 90°.
	c = 37.805(9) Å	γ = 90°.
Volume	5393(2) Å^3	
Z	8	
Density (calculated)	1.470 Mg/m^3	
Absorption coefficient	0.403 mm^{-1}	
F(000)	2432	
Crystal size	0.60 x 0.16 x 0.08 mm^3	
θ range for data collection	2.047 to 22.534°.	
Index ranges	-7<=*h*<=7, -21<=*k*<=21, -40<=*l*<=40	
Reflections collected	8389	
Independent reflections	3545 [R_{int} = 0.1049]	
Completeness to θ = 22.534°	99.9 %	
Absorption correction	ψ-scans (0.213 – 0.245)	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3545 / 53 / 399	
Goodness-of-fit on F^2	1.092	
Final *R* indices [*I*>2σ(*I*)]	R_1 = 0.0621, wR_2 = 0.1472	
R indices (all data)	R_1 = 0.1109, wR_2 = 0.1848	
Extinction coefficient	0.00053(17)	
Largest diff. peak and hole	0.409 and -0.284 e.Å^{-3}	

Table S27. Hydrogen bonds for **4** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1)-H(1A)...N(12)	0.93	2.59	3.410(8)	146.9
C(4)-H(4A)...O(20B)	0.93	1.95	2.667(13)	132.5
C(5)-H(5A)...N(18A)	0.93	2.63	3.182(16)	118.6
C(5)-H(5A)...O(20A)	0.93	2.00	2.72(3)	132.8
C(8)-H(8A)...N(14)	0.93	2.63	3.442(8)	146.2
C(26)-H(26A)...O(23)#1	0.93	2.63	3.268(8)	126.2
C(31)-H(31A)...O(16)#2	0.93	2.65	3.489(9)	150.8
C(32)-H(32A)...O(19A)#3	0.93	2.33	3.25(2)	169.2
C(32)-H(32A)...O(20A)#3	0.93	2.52	3.241(18)	134.5
C(37)-H(37A)...O(35)#4	0.96	2.52	2.99(6)	110.4
C(37)-H(37B)...O(16)#5	0.96	2.11	3.00(4)	152.5

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1 #2 x-1/2,y,-z+1/2 #3 -x+1/2,y-1/2,z
#4 x+1/2,y,-z+1/2 #5 -x+3/2,y+1/2,z

In the acceptor molecule, nitro group bonded to C4 is disordered over two positions, N18A/O19A/O20A [sof = 0.365(10)] and N18B/O19B/O20B [sof = 1 - 0.365(10) = 0.635(10)], emulating the C_2 local symmetry for this molecule. The geometry of these nitro groups was restrained as in isomorphous complex **3**.
Acetone is strongly disordered and was modelled with a single position with fully restrained geometry: C34–C36 and C34–C37 bond lengths were restrained to 1.46(1) Å, and C36…C37 separation to 2.51(2) Å. Carbonyl bond length was restrained to C34–O35 = 1.20(1) Å and the whole molecule was restrained to be flat (standard *FLAT* command in *SHELXL*). Finally, ADP's for acetone were restrained to be similar and approximate an isotropic behaviour (standard *SIMU* and *ISOR* commands in *SHELXL*). All H atoms were included in calculated positions and refined as riding to their carrier C atoms.



Alert level A

THETM01_ALERT_3_A	The value of sine(theta_max)/wavelength is less than 0.550
	Calculated sin(theta_max)/wavelength = 0.5392

Author Response: Poor diffraction, probably related to solvent loss Poor diffraction, probably related to solvent loss

Alert level C

REFNR01_ALERT_3_C	Ratio of reflections to parameters is < 10 for a centrosymmetric structure	
	sine(theta)/lambda	0.5392
	Proportion of unique data used	1.0000
	Ratio reflections to parameters	8.8847
PLAT031_ALERT_4_C	Refined Extinction Parameter within Range	3.118 Sigma
PLAT088_ALERT_3_C	Poor Data / Parameter Ratio	8.88 Note
PLAT213_ALERT_2_C	Atom O19A has ADP max/min Ratio	3.5 prolat
PLAT213_ALERT_2_C	Atom N18A has ADP max/min Ratio	3.1 oblate
PLAT220_ALERT_2_C	Large Non-Solvent O Ueq(max)/Ueq(min) Range	3.3 Ratio
PLAT234_ALERT_4_C	Large Hirshfeld Difference O19B -- N18B ..	0.20 Ang.
PLAT234_ALERT_4_C	Large Hirshfeld Difference N18B -- C5 ..	0.16 Ang.
PLAT340_ALERT_3_C	Low Bond Precision on C-C Bonds	0.0082 Ang.
PLAT480_ALERT_4_C	Long H...A H-Bond Reported H26A .. O23 ..	2.63 Ang.
PLAT480_ALERT_4_C	Long H...A H-Bond Reported H31A .. O16 ..	2.65 Ang.
PLAT906_ALERT_3_C	Large K value in the Analysis of Variance	2.743 Check
PLAT911_ALERT_3_C	Missing # FCF Refl Between THmin & STh/L= 0.539	4 Report

Fig. S28 ORTEP view of complex **4** (asymmetric unit; 20% probability level) and checkCIF/PLATON report (Alert level G omitted)

Table S29. Crystal data and structure refinement for complex **5**

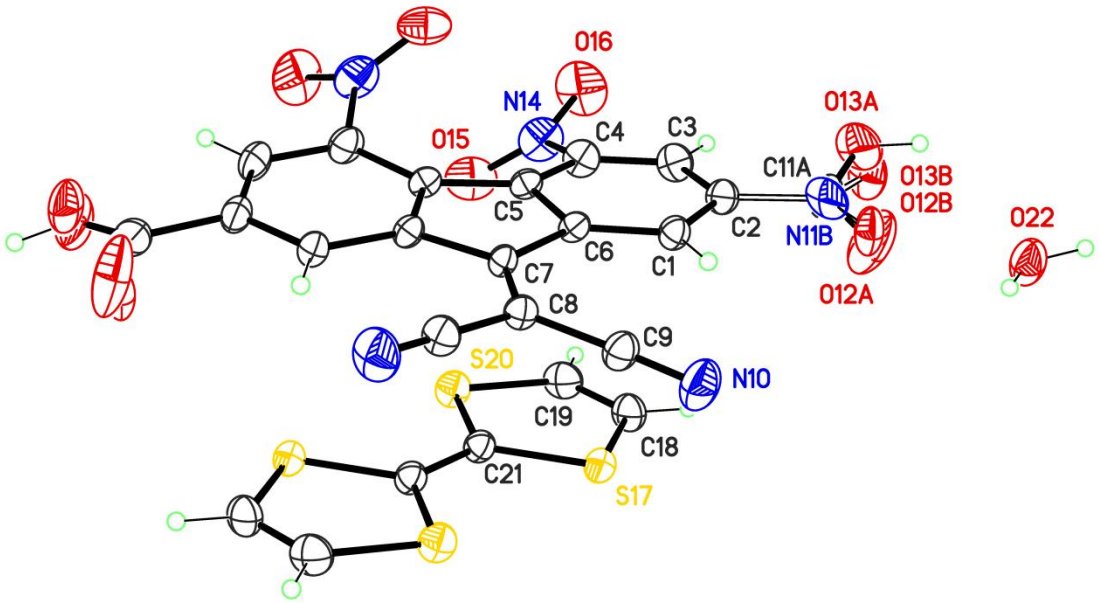
Identification code	**(TTF-DC2TF).H_2O**	
Empirical formula	C_{23} H_{11} N_5 O_9 S_4	
Formula weight	629.61	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	*a* = 15.9432(14) Å	α= 90°.
	b = 12.1351(9) Å	β= 104.572(7)°.
	c = 13.5738(11) Å	γ = 90°.
Volume	2541.7(4) Å^3	
Z	4	
Density (calculated)	1.645 Mg/m^3	
Absorption coefficient	0.439 mm^{-1}	
F(000)	1280	
Crystal size	0.60 x 0.34 x 0.20 mm^3	
θ range for data collection	2.135 to 27.499°.	
Index ranges	-20<=*h*<=13, -15<=*k*<=15, -17<=*l*<=17	
Reflections collected	6560	
Independent reflections	2918 [R_{int} = 0.0256]	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	ψ-scans (0.286 – 0.336)	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2918 / 14 / 227	
Goodness-of-fit on F^2	1.064	
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0547, wR_2 = 0.1448	
R indices (all data)	R_1 = 0.0647, wR_2 = 0.1511	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.912 and -0.390 e.Å^{-3}	

Table S30. Hydrogen bonds for **5** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(13A)-H(13A)...O(22)	0.88(2)	2.41(6)	3.03(2)	128(6)
O(22)-H(22A)...O(15)#3	0.85(2)	2.18(6)	2.944(6)	150(11)
O(22)-H(22A)...O(22)#4	0.85(2)	2.41(10)	2.869(14)	115(9)
O(22)-H(22B)...O(12A)#4	0.85(2)	1.85(3)	2.697(19)	173(11)
O(22)-H(22B)...O(12B)#4	0.85(2)	1.85(4)	2.682(11)	167(12)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+3/2 #2 -x+1,-y+1,-z+1 #3 -x+3/2,y-1/2,-z+3/2
#4 -x+2,-y+1,-z+2

The acceptor molecule is placed on the twofold crystallographic axis in *C*2/*c* space group and has then substituents bonded at C2 and C2' disordered (carboxylic group C11A/O12A/O13A/H13A and nitro group N11B/O12B/O13B, both with sof's constrained by symmetry to ½). The carboxylic group was restrained to a sensible geometry: C2–C11A = 1.49(2) Å, C11A–O12A = 1.22(2) Å, C11A–O13A = 1.30(4) Å, O12A...O13A = 2.22(4) Å, O13A–H13A = 0.88(2) Å and O12A...H13A = 2.35(4) Å. The carboxylic acid group was restrained to be flat (standard *FLAT* command in *SHELXL*). The geometry of the disordered nitro group was also restrained: C2–N11B = 1.47(2) Å, N–O bond lengths = 1.21(2) Å, and O12B...O13B = 2.15(4) Å. The TTF molecule is placed across an inversion centre and was refined freely. For the *DA* complex, C-bonded H atoms were included in calculated positions and refined as riding to their carrier C atoms. The hydroxyl H atom H13A was first located in a difference map, and its position geometrically restrained as described above. The water molecule O22 is placed close to an inversion centre, and was refined with sof constrained to ½. H atoms H22A and H22B were first found in a difference map, and the geometry of the water molecule was eventually restrained with O–H bond lengths = 0.85(2) Å and H...H separation = 1.35(4) Å. C-bonded H atoms were included in calculated positions and refined as riding to their carrier atoms.



Alert level B

PLAT782 ALERT 2 B	Unusual Bond Geometry for C-NO2 Moiety Around N14	Check

Alert level C

PLAT094 ALERT 2 C	Ratio of Maximum / Minimum Residual Density	2.34	Report
PLAT215 ALERT 3 C	Disordered N11B has ADP max/min Ratio	3.2	
PLAT340 ALERT 3 C	Low Bond Precision on C-C Bonds	0.0041	Ang.
PLAT906 ALERT 3 C	Large K value in the Analysis of Variance	4.577	Check
PLAT911 ALERT 3 C	Missing # FCF Refl Between THmin & STh/L= 0.600	3	Report
PLAT975 ALERT 2 C	Check Calcd Residual Density 1.05A From O15	0.83	eA-3

Fig. S31 ORTEP view of complex **5** (30% probability level) and checkCIF/PLATON report (Alert level G omitted). Unlabelled atoms are generated by symmetry operators 1-*x*, *y*, 3/2-*z* (DC_2TF molecule) and 1-*x*, 1-*y*, 1-*z* (TTF molecule).

Table S32. Crystal data and structure refinement for complex **6**

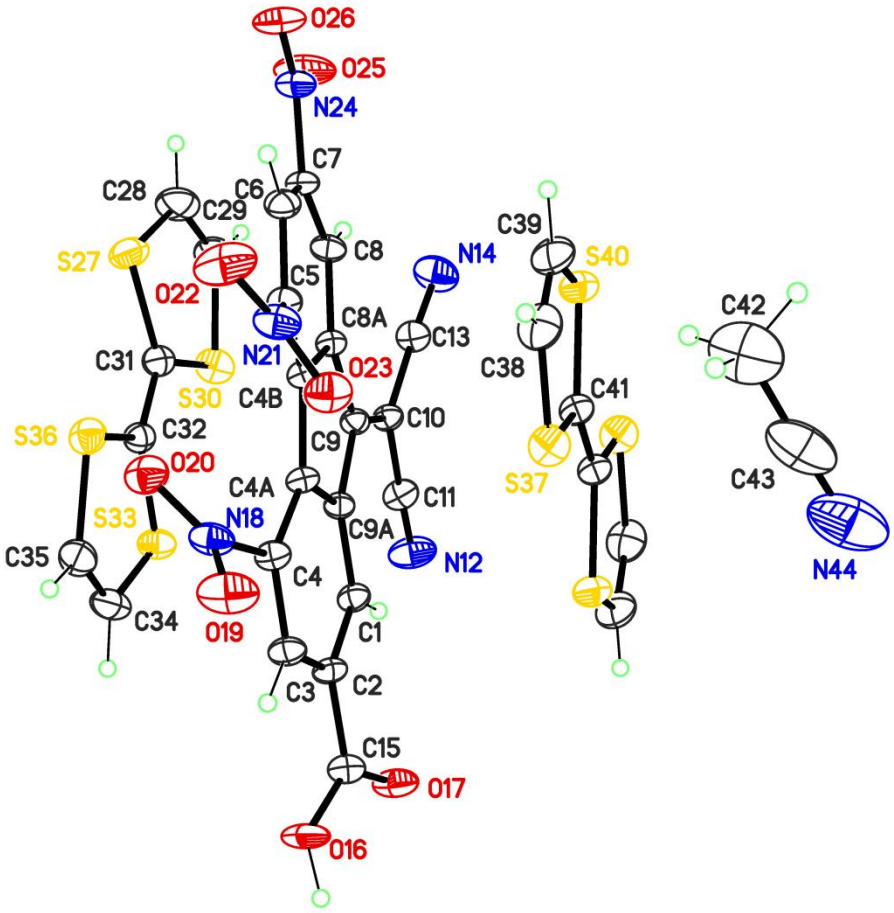
Identification code	**$(TTF)_3(DC2TF)_2.2CH_3CN$**	
Empirical formula	$C_{56}\ H_{28}\ N_{12}\ O_{16}\ S_{12}$	
Formula weight	1509.62	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 10.0608(10) Å	α= 107.535(8)°.
	b = 10.3528(11) Å	β= 100.525(9)°.
	c = 15.612(2) Å	γ = 90.877(8)°.
Volume	1520.2(3) $Å^3$	
Z	1	
Density (calculated)	1.649 Mg/m^3	
Absorption coefficient	0.513 mm^{-1}	
F(000)	768	
Crystal size	0.40 x 0.40 x 0.24 mm^3	
θ range for data collection	2.065 to 25.000°.	
Index ranges	-11<=*h*<=1, -11<=*k*<=11, -18<=*l*<=18	
Reflections collected	6125	
Independent reflections	5172 [R_{int} = 0.0467]	
Completeness to θ = 25.000°	96.9 %	
Absorption correction	ψ-scans (0.349 – 0.393)	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5172 / 1 / 437	
Goodness-of-fit on F^2	1.059	
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0569, wR_2 = 0.1385	
R indices (all data)	R_1 = 0.0862, wR_2 = 0.1567	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.413 and -0.354 $e.Å^{-3}$	

Table S33. Hydrogen bonds for **6** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(6)-H(6A)...S(33)#2	0.93	2.99	3.908(4)	169.5
C(8)-H(8A)...N(14)	0.93	2.58	3.364(6)	142.6
O(16)-H(16)...O(17)#3	0.951(10)	1.748(13)	2.697(4)	175(6)
C(28)-H(28A)...O(25)#4	0.93	2.60	3.274(6)	130.0
C(34)-H(34A)...N(44)#5	0.93	2.51	3.239(8)	135.5
C(35)-H(35A)...N(14)#6	0.93	2.59	3.470(6)	157.4
C(39)-H(39A)...N(12)#2	0.93	2.46	3.343(7)	159.1
C(42)-H(42B)...O(22)#7	0.96	2.66	3.452(9)	140.2

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z+2 #2 x+1,y,z #3 -x-1,-y+1,-z+2
#4 -x,-y-1,-z+1 #5 -x,-y+1,-z+2 #6 x,y+1,z #7 -x+1,-y+1,-z+2

Refinement for this complex was standard and carried out without restrictions nor constrictions. All H atoms were included in calculated positions and refined as riding to their carrier C atoms.



Alert level C

PLAT029_ALERT_3_C	_diffrn_measured_fraction_theta_full Low	0.969 Note
PLAT244_ALERT_4_C	Low 'Solvent' Ueq as Compared to Neighbors of	C43 Check
PLAT340_ALERT_3_C	Low Bond Precision on C-C Bonds	0.0066 Ang.
PLAT480_ALERT_4_C	Long H...A H-Bond Reported H6A .. S33 ..	2.99 Ang.
PLAT480_ALERT_4_C	Long H...A H-Bond Reported H42B .. O22 ..	2.66 Ang.
PLAT906_ALERT_3_C	Large K value in the Analysis of Variance	3.274 Check
PLAT911_ALERT_3_C	Missing # FCF Refl Between THmin & STh/L= 0.595	133 Report

Fig. S34 ORTEP view of complex **6** (30% probability level) and checkCIF/PLATON report (Alert level G omitted). Unlabelled atoms in one TTF molecule are generated by symmetry operator *-x*, *-y*, 2-*z*